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(54) Title: LITHOGRAPHIC PLATE			
(57) Abstract			
<p>There is described a method of forming a lithographic plate by the heat-mode imaging method which comprises coating on a base which can be used as a lithographic base, a positive working photosensitive composition which comprises a naphthoquinone diazide ester of a phenolic resin or a naphthoquinone diazide ester and a phenolic resin and at least one substance which absorbs infrared radiation, overall exposing the assembly to ultraviolet light to render the photosensitive composition developable, imaging the plate by means of a laser which emits in the infrared region of the spectrum and then developing the plate to remove those areas of the photosensitive composition not exposed to the laser.</p>			

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Lithographic Plate

It is becoming of increasing interest to image lithographic plates digitally by use of a laser. A number of prior art methods have been proposed wherein an infra-red emitting laser is used. The laser light is converted to heat by the presence in the photosensitive composition of an infra-red absorbing substance. Examples of such prior art methods are described in E.P. 625728, US 4132168, E.P. 580393, E.P. 599510, US 3707372 and US 3619157. However, a number of the prior art methods as proposed in the patents involve the formation of a mask in the assembly. This is difficult to achieve and often leads to a lengthy processing sequence to develop the printing image. A large number of the prior art methods as proposed in the patents require the use of unusual photosensitive compositions of the type not used in lithography. These require special formulation techniques, special coating techniques and also special processing techniques. Not surprisingly, as far as it is known, many such methods have never been commercialised. Other methods described in the prior art patents require an assembly having several layers thus increasing the cost of preparing the lithographic plate.

We have discovered a method of digitally imaging a lithographic plate with a laser using a photosensitive compound which has been widely used for the preparation of lithographic plates.

Therefore according to the present invention there is provided a method of forming a lithographic plate by the heat-mode imaging method which comprises coating on a base which can be used as a lithographic base a positive working photosensitive composition which comprises a naphthoquinone diazide ester of a phenolic resin or a naphthoquinone diazide ester and a phenolic resin and at least one substance which absorbs infra-red radiation, overall exposing the assembly to ultra-violet light to render the photosensitive composition developable, imaging the plate by means of a laser which emits in the

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infra-red region of the spectrum and then developing the plate to remove those areas of the photosensitive composition not exposed to the laser.

This invention is based on the knowledge that when light-exposed naphthoquinone diazide compound is heated it is no longer developable. In the method of the present invention after overall exposure to U.V. light to render it developable the naphthoquinone diazide compound is image-wise heated to render such areas non-developable by the action of the laser which emits in the infra-red region of the spectrum and the presence of the infra-red absorbing substance or substances which convert the infra-red laser light to heat. Thus after the development step the areas of the initially light sensitive naphthoquinone diazide compound which remain on the plate are oleophilic and form the printing image whilst the areas of the plate from which the photosensitive composition has been removed from the hydrophilic areas of the plate.

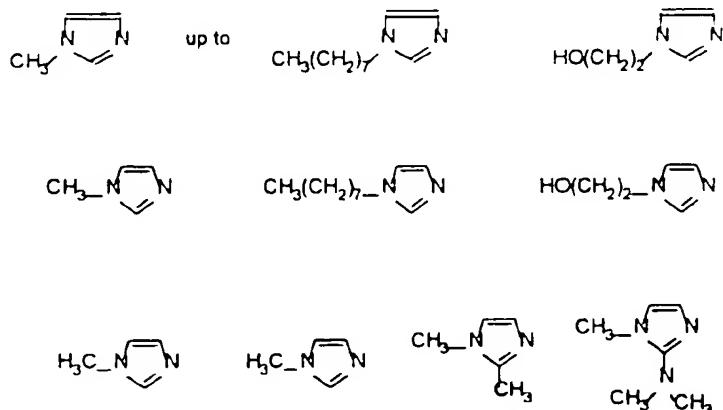
The binder for the photosensitive composition is the phenolic resin. This may be present covalently bonded to the naphthoquinone moiety or it may be present not bonded to the moiety. The preferred phenolic resins are novolak resins and resole resins.

The preferred naphthoquinone diazide esters are a o-naphthoquinone diazide sulphonic acid or a o-naphthoquinone diazide carboxylic acid ester.

Most preferably there is present in the photosensitive composition a substance which lowers the temperature at which the exposed naphthoquinone diazide compound is rendered no longer developable. Examples of such compounds are basic compounds for example amine, for instance ethanolamine or methanolamine. Useful basic compounds are imidazoles.

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Examples of suitable imidazoles compound are:-



Imidazoline compounds and in particular 1-hydroxyethyl- 2-alkylimidazoline where the alkyl substituent has 7 to 17 carbon atoms can also be used.

Other compounds which may be used to lower the temperature at which the naphthoquinone diazide compound is rendered no longer developable are certain dyes for example Oilsol yellow and disperse black.

If strongly acid substances or strong-acid generators are present in the photosensitive composition their presence tends to prevent the exposed naphthoquinone diazide compound from becoming undevelopable when heated. Therefore their presence in the photosensitive composition is to be deprecated.

Usefully a dye may be present which helps to locate the image areas after the development step. An example of a suitable dye is a triarylmethane dye. Particularly suitable are ones that are of basic character.

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Examples of o-naphthoquinone diazide compounds which may be used in the photosensitive composition are disclosed in a variety of publications such as U.S. Pat. Nos. 2,766,118; 2,767,092; 2,772,972; 2,859,112; 2,907,665; 3,046,110; 3,046,111; 3,046,115; 3,046,118; 3,046,119; 3,046,120; 3,046,121; 3,046,122; 3,046,123; 3,061,430; 3,102,809; 3,106,465; 3,635,709; and 3,647,443. Among these, particularly preferred are o-naphthoquinonediazidosulfonates or o-naphthoquinone-diazidocarboxylates of aromatic hydroxyl compounds; o-naphthoquinone-diazidosulfonic acid amides or o-naphthoquinonediazidocarboxylic acid amides of aromatic amine compounds, for instance, esters of naphthoquinone-1, 2-diazidosulfonic acid with polyhydroxyphenyl (hereinafter the term 'ester' also include partial esters); esters of naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1, 2-diazido-5-sulfonic acid with pyrogallol/acetone resins; esters of naphthoquinone-1, 2-diazidosulfonic acid with novolac type phenol/formaldehyde resins or novolac type cresol/formaldehyde resins; amides of poly(p-aminostyrene) and naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1, 2-diazido-5-sulfonic acid; esters of poly(p-hydroxystyrene) and naphthoquinone-1, 2-diazido-5-sulfonic acid; esters of polyethylene glycol with naphthoquinone-1, 2-diazido-4-sulfonic acid or naphthoquinone-1, 2-diazido 5-sulfonic acid; amides of polymeric amines with naphthoquinone-1, 2-diazido-4-sulfonic acid.

Thus when the preferred o-naphthoquinone diazide compounds are used such as o-naphthoquinone diazide sulphonates or o-naphthoquinone diazido-carboxylates they are present covalently bonded to resins. Thus no additional binder is required.

The infra-red absorbing compound may be carbon such as carbon black or graphite. It may be a commercially available pigment such as Heliogen Green as supplied by BSAF or Nigrosine Base NG1 as supplied by N H Laboratories Inc. Usefully it may be an organic pigment or dye such as phthalocyanine pigment. Or it may be a dye or pigment

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of the squarylium, cyanine, merocyanine, indolizine, pyrylium or metal dithioline classes.

Preferably the infra-red absorbing compound is one whose absorption spectrum is significant at the wavelength output of the laser which is to be used in the method of the present invention. For example gallium arsenide diode lasers emit at 830nm and Nd YAG lasers emit at 1064nm.

Thus the preferred photosensitive composition for use in the method of the present invention comprises a 2,4-naphthoquinone diazide sulphonic acid ester of a novolac resin, an infra-red absorbing compound, a basic colourant dye and an imidazole.

Preferably neither the colourant dye nor any other substance in the composition have significant light absorption at the wavelength of the ultra-violet light used for the initial overall exposure. This wavelength is preferably between 350-450nm.

Preferably in the lithographic assembly used in the method of the present invention there is present between the photosensitive layer and the base a heat insulator layer which attenuates the thermal conductivity to the base. This is especially useful if the base is an aluminium plate base. In the preparation of an aluminium plate base for use in lithography there usually forms on the base a thin layer of aluminium oxide which is often between 2 to 3 microns in thickness. However, in some methods of preparing the base a layer of aluminium oxide is formed which is from 10 to 15 microns in thickness. Such a thickness of aluminium oxide acts very efficiently as a heat insulation layer. However, if the thickness of the aluminium oxide layer is much greater than 15 microns an unstable layer can be formed which tends to flake off.

*(a polymer)
2 microns*

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Thermal conduction from the imaging layer may also be reduced by optimisation of anodising conditions to produce an anodic sub-layer of low porosity and low thermal conductivity.

Thermal conduction from the imaging layer may also be reduced by use of hydrophilising layers such as those described in E.P.A. 626273.

Preferably as much infra-red absorber is present in the photosensitive composition so as not to interfere with the photochemical U.V. exposure step. Dyes with the selective IR absorption can be present in a greater amount than a black body such as carbon.

By having a thermal insulating layer and by varying the amount of infra-red absorber present in the photosensitive composition it is possible to minimise the loss of resolution through lateral heat conductivity whilst maintaining sufficient sensitivity.

The base which can be used as a lithographic base is preferably an aluminium plate which has undergone the usual anodic, graining and post-anodic treatments well known in the lithographic art for enabling a photosensitive composition to be coated thereon.

Another base material which may be used in the method of the present invention is a plastics material base or a treated paper base as used in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been subbed to render its surface hydrophilic. A so-called resin coated paper which has been corona discharge treated may also be used.

In the method of the present invention the lithographic plate after coating and drying down is overall exposed to a conventional U.V. radiation source such as a carbon arc lamp, a mercury vapour lamp, a fluorescent lamp, a tungsten filament lamp or a

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photoflood lamp just prior to thermal imaging. It is an advantage of the method as herein described that a combination of a light exposure and heating steps is required to form the image. In this way materials may be designed which have a low energy requirement for thermal imaging without the usually associated problems of shelf life limited by variations of temperature during storage

An example of a suitable practical developing solution is an aqueous solution of 8% metasilicate, 0.1% of an organic phosphate ester of an ethoxylated alcohol and 0.01% of polyoxylpropylene methyl ethyl ammonium chloride.

LASER IMAGING

The coated substrate to be imaged was cut into a circle of 105mm diameter and placed on a disc that could be rotated at a constant speed of 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged normal to the coated substrate, while the translating table moved the laser beam radially in a linear fashion with respect to the spinning disk. The exposed image was in the form of a spiral whereby the image in the centre of the spiral represented slow laser scanning speed and long exposure time and the outer edge of the spiral represented fast scanning speed and short exposure time.

The laser used was a single mode 830nm wavelength 200mW laser diode which was focused to a 10 micron resolution. The laser power supply was a stabilised constant current source.

PROCESSING AFTER IMAGING

The exposed disc was developed by immersing in the alkaline developer solution which removed the non-imaged coating leaving the exposed spiral image. The larger the diameter of the resulting spiral image corresponded to the less exposure time required to

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form the image. Exposure time quoted in the examples was the calculated time required for the laser to pass over a theoretical 10 micron square on the surface of the substrate and corresponded to an exposure sufficient to produce an image line that resisted the developer treatment.

CONVENTIONAL IMAGING

It is to be understood, that the plate precursors prepared in the present invention can also be U.V. imaged to yield a positive working plate or can be reversal imaged to yield a negative working plate.

DEVELOPERS

Different coatings had different alkali solubility and required different developer compositions. Below are the basic compositions of the three developers used in the examples.

Developer A

3% Sodium Metasilicate pentahydrate in water.

Developer B

7% Sodium Metasilicate pentahydrate in water.

Developer C

14% Sodium Metasilicate pentahydrate in water.

The imaged substrate was developed for 30 seconds.

MATERIALS

The following substances were used in the examples which follow.

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Disperse Black 3
Oilsol Yellow DEA

The triaryl methane dye used was:- Basonlyl Violet 610

IR dye 950609-1A

IR dye I-1-9L

IR dye NK1887

IR dye NK2014

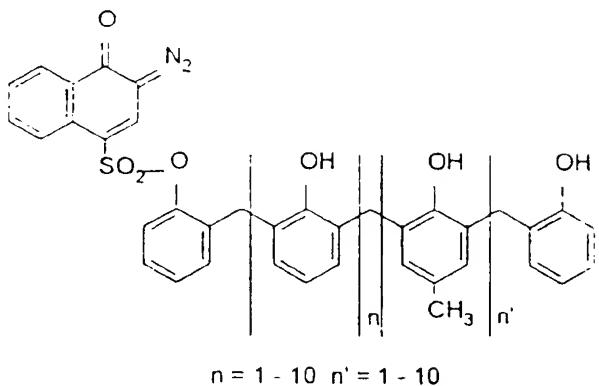
Resin Uravar FN6

Carbon Black

Bakelite novolak resins

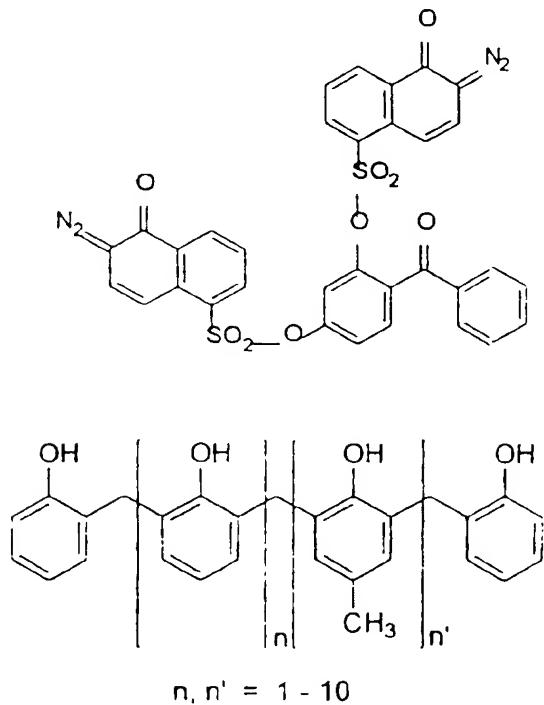
- 10 -

The 214 NQD resin ester used in the examples was based on novolak resins . Shown in the examples as 214-NQD resin ester A



214 NQD PHENOL/CRESOL NOVOLAK RESIN ESTER A

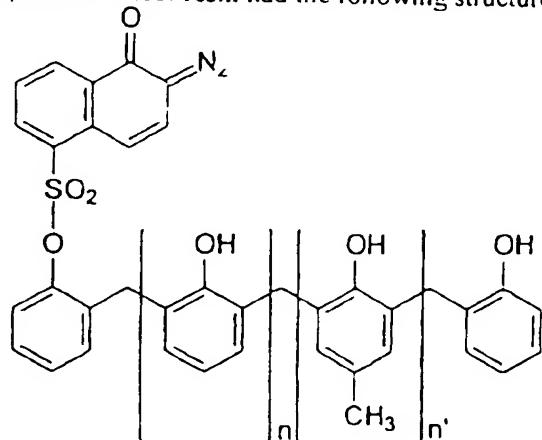
The bis 215 NQD ester of dihydroxybenzophenone had the following structure -



PHENOL/CRESOL NOVOLAK RESIN

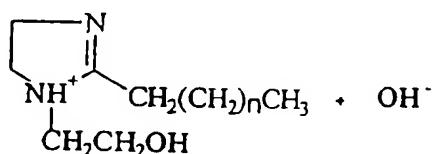
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The 215 NQD ester of phenol / cresol resin had the following structure:-



$$n, n' = 1 - 10$$

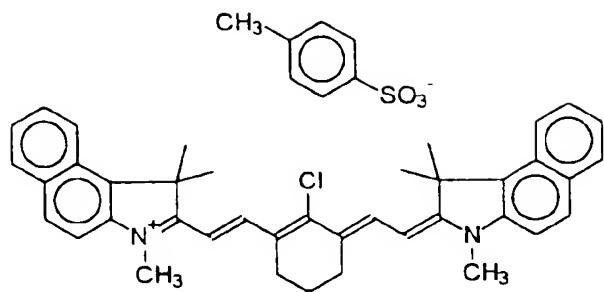
Monazoline C, the temperature lowering basic compound had the following structure:-



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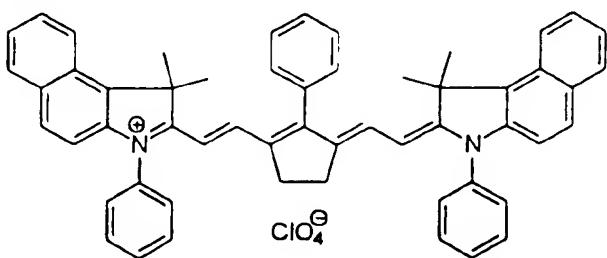
The IR dyes used have the following structures:-

DYE 950609-1A

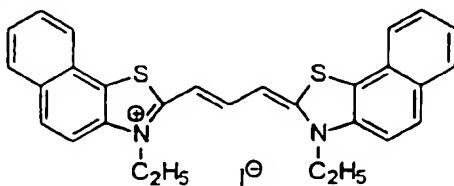


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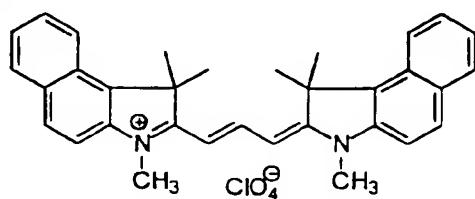
I-1-9L



NK1887



NK2014



The following Examples will serve to illustrate the invention.

EXAMPLES

Composition 1

A mixture containing 214 NQD resin ester A, Monazoline C, infrared absorbing dye 950609-1A and Dowanol PM solvent was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electro-grained and anodised, giving a coating film weight of 1.3 gm per sq. metre after thoroughly drying at 100°C in an oven for 3 minutes.

The resulting plate was flood exposed in a light frame using a 3kw mercury halogen lamp for 90 seconds at a distance of 1 metre.

The plate was then imaged using a 200mW laser diode at a wavelength of 830nm using the imaging device described previously. The plate was then developed using the alkaline developer B for 30 seconds which removed the parts of the coating on the plate that were not struck by the laser beam, giving an image

Composition 2

A mixture containing a solution of 214 NQD resin A, a solution of Disperse black, an infrared absorbing dye 950609-1A and Dowanol PM was coated onto an aluminium substrate as in Composition 1 with a film weight of 1.46 gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 3

A mixture containing a solution of 214 NQD resin ester A, Oilsol Yellow DEA, an infrared absorbing dye ref. 950609-1A and Dowanol PM solvent, was coated onto an aluminium substrate as in Composition 1 giving a film weight of 1.3 gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 4

A mixture containing phenol/cresol novolak resin in Dowanol PM, and bis 215 NQD ester of dihydroxybenzophenone, Monazoline C and IR dye ref. 950609-1A was coated onto an aluminium substrate as in Composition 1 with a film weight of 1.4 gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 5

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A solution containing a phenol/cresol novolak resin and bis 215 NQD ester of dihydroxybenzophenone, Monazoline C, infrared dye ref. 950609-1A and Dowanol PM was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.35 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 6

A mixture containing a 215 NQD ester of a phenol/cresol novolak resin , Monazoline C, infrared absorbing dye ref. 950609- 1A, and Dowanol PM solvent, was coated onto an aluminium as in Composition 1 with a film weight of 1.48 gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 7

A solution containing 214 NQD resin ester A into which was dispersed carbon black, Monazoline C and Dowanol PM was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.22 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 8

A mixture containing 214 NQD resin ester A, Monazoline C, IR dye NK1887 and Dowanol PM was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.27 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 9

A solution containing 214 NQD resin ester A, in Dowanol PM, Monazoline C, IR dye NK 2014 and Dowanol PM, was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.3 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 10

A solution containing 214 NQD resin ester A,Monazoline C, IR dye I-1-9L and Dowanol PM, was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.3 gm per square

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metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 11

A solution containing Uravar FN6 resole resin, Monazoline C, bis 215 NQD ester of dihydroxybenzophenone, IR DYE 950609-1A and Dowanol PM, was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 2.5 gm per sq. metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 12

A solution containing 214 NQD resin ester A into which was dispersed carbon black, and Dowanol PM was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.3 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 13

A mixture containing 214 NQD resin ester A, Triethanolamine, infra red absorbing dye ref. 950609-1A and Dowanol PM solvent was coated onto an aluminium substrate as in Composition 1 with a film weight of 1.3gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 14

A mixture containing 2.81 gm of a 40% solution of 214 NQD resin ester A, aminomethylpropanol, an infra red absorbing dye Ref. 950609-1A and Dowanol PM solvent was coated onto an aluminium substrate as in Composition 1 with a film weight of 1.32 gm per square metre. When imaged and processed as in Composition 1 the plate performed in the same manner.

Composition 15

A mixture containing 214 NQD resinester of Bakelite resins, Monazoline C, Basonyl violet 620, IR dye 950609-1A and Dowanol PM was prepared and coated onto a substrate consisting of a sheet of aluminium that had been electrograined and anodised, giving a coating film weight of 1.33 gm per square metre after thoroughly drying at 100°C in an oven for 3 minutes. When imaged and processed as in Composition 1 the plate performed in the same manner.

The plates as illustrated by all the examples were inked-up and printed. In every case over 10,000 good copies were prepared.

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The run length of all the examples can be extended by baking between 200°C and 300°C. An added advantage of the invention is that a lithographic plate of the examples could be imaged conventionally with a UV light source to produce a conventional positive plate or a negative plate via the process described in Patent GB 2 082 339.

As the claimed invention relies on a heating process, any suitable light of sufficient power and is suitably absorbed by components in the system to generate heat in the composition, could be used.

TABLE OF COMPOSITIONS AND RESULTS

Composition number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
214 NQD resin ester A	91	95	95				76	77	87	89		80	91	93.5	91
215 NOD resin ester				20	30	95					30				
Bis 215 NQD ester				71	61						61				
Pheno/cresol novolak resin															
Uravar resol resin															
Monazoline C	5			5	5	1	5	5	5	5	5			2.5	4
Aminomethylpropanol													5		
Triethanolamine															
Disperse black 3		1		1											
Oilsol yellow DEA															
IR DYE 950609-1A	4	4	4	4	4	4	19				4	20	4	4	4
Carbon black							18		8						
IR Dye NK1887															
IR Dye NK2014															
IR Dye I-1-9L											6				
Basonyl Violet 620															1
Developer	B	A	A	B	A	A	C	B	B	B	B	B	A	A	B
Coating Weight (gm/sq.metre)	1.3	1.46	1.3	1.4	1.35	1.48	1.22	1.27	1.3	1.3	1.18	1.3	1.3	1.32	1.33
Exposure requirement (microseconds)	6	11	11	3	2	6	5	8	2	3	2	32	10	7	6

Comparison of compositions 7 and 12 show the effect of the addition of Monazoline, showing that less energy is required to form a developable image.

The addition of basic materials both increase the thermal energy sensitivity and modify development characteristics. It is therefore necessary to choose an appropriate developer for best discrimination between image and non image areas.

Comparing compositions 2 and 3 to composition 12 show that basic dyes increase the sensitivity. Note the use of a colourant dye in composition 15.

Claims:-

1. A method of forming a lithographic plate by the heat-mode imaging method which comprises coating on a base which can be used as a lithographic base a positive working photosensitive composition which comprises a naphthoquinone diazide ester of a phenolic resin or a naphthoquinone diazide ester and a phenolic resin and at least one substance which absorbs infra-red radiation, overall exposing the assembly to ultra-violet light to render the photosensitive composition developable, imaging the plate by means of a laser which emits in the infra-red region of the spectrum and then developing the plate to remove those areas of the photosensitive composition not exposed to the laser.
2. A method according to claim 1 wherein the naphthoquinone diazide ester is a 0-naphthoquinone diazide sulphonic acid or 0-naphthoquinone diazide carboxylic acid ester.
3. A method according to claim 1 wherein the phenolic resin is a novolac resin or a resole resin, or a mixture of the two.
4. A method according to claim 1 wherein there is present in the positive working photosensitive composition a substance which lowers the temperature at which the exposed naphthoquinone diazide compound is rendered no longer developable.
5. A method according to claim 4 wherein the temperature lowering substance is a basic substance.
6. A method according to claim 5 wherein the basic substance is an imidazole or an amine.

7. A method according to claim 6 wherein the imidazoline compound is 1-hydroxyethyl-2-alkylimidazoline where the alkyl substituent has 7 to 17 carbon atoms.
8. A method according to claim 4 wherein the temperature lowering substance is a dye.
9. A method according to claim 8 wherein the dye is Oilsol yellow or disperse black.
10. A method according to claim 1 wherein the infra red absorbing substance is carbon black, a pigment or a dye.
11. A method according to claim 10 wherein the dye is NK1887, NK2014 or I-1-9L
12. A method according to claim 1 wherein there is present between the photosensitive layer and the base a heat insulating layer.
13. A method according to claim 12 wherein the heat insulating layer is a layer of aluminium oxide from 1 to 15 microns thickness.
14. A method according to claim 1 wherein the preferred base which can be used as a lithographic base is an aluminium plate which has undergone the usual anodic, graining and post-anodic treatment for enabling a photosensitive composition to be coated thereon.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 95/02774

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/022 B41C1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F B41C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 544 627 (TAKAHASHI YONOSUKE ET AL) 1 October 1985 see column 3, line 59 - column 4, line 26 see column 4, line 54 - column 5, line 14 see column 5, line 15 - column 6, line 2 see column 15, line 19 - line 24 see column 20, line 20 - line 24 see column 20, line 45 - column 21, line 56 ---	1-14
A	US,A,5 340 699 (N.F. HALEY) 23 August 1994 cited in the application (corresponds to EP-A-625728) ---	
A	EP,A,0 293 656 (HOECHST AG) 7 December 1988 ---	-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

5 March 1996

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Entered Application No
PCT/GB 95/02774

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	DE,A,44 26 820 (FUJI PHOTO FILM CO LTD) 2 February 1995 see the whole document -----	1-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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